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2,898,262

COMPOSITIONS AND METHODS

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This invention relates to certain alkyl mercury salts of polyamine acetic acids and to fungicidal compositions and methods employing these compounds for the protection of organic matter subject to fungus infection.

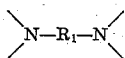
Recently a number of organo mercury fungicides have been made commercially available. Certain of these compounds have outstanding fungicidal activity for certain uses such as for treating seeds. However, none of these organo mercury fungicides have proven entirely satisfactory. Most of these compounds are insoluble in aqueous medium, and therefore must be formulated with some type of fungicidal adjuvant or carrier material. These few organo-mercury fungicides that are sufficiently water-soluble for application from an aqueous medium have in many cases proven to be relatively phytotoxic, and for this reason are not completely satisfactory.

It is therefore apparent that there is a real need for an improved water-soluble organomercury fungicide of high anti-fungal activity.

In accordance with the present invention, certain alkyl mercury salts of polyamine acetic acids have been discovered that are water-soluble, have high fungicidal activity, and appear to be of outstandingly low phytotoxicity at use levels.

The compounds of the present invention are alkyl-mercury salts of polyamine acetic acids wherein the polyamine group is of the general structure.

(1)



in which R_1 is selected from the group consisting of divalent saturated hydrocarbon groups of from 2 through 12 carbon atoms, and divalent saturated aliphatic chains consisting of from 4 through 12 carbon atoms and from one through 5 nitrogen atoms with each nitrogen atom dividing the chain into alkylene groups of not less than 2 carbon atoms each; at least one valence of a polyamine nitrogen being satisfied by an alkylmercury acetate group of the type $-\text{CR}_2\text{R}_3\text{COOHgR}_4$ in which R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups, and R_4 is an alkyl group; and the remainder of the valences of the polyamine nitrogens being satisfied

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by radicals selected from the group consisting of hydrogen, alkyl groups, hydroxyalkyl groups and



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in which R_2 and R_3 have the significance set forth above and Y is selected from the group consisting of hydrogen, alkali metal cations, ammonium or substituted amine.

10 The better compounds of the present invention, from the standpoint of ease and economy of preparation and usage, are those wherein R_2 and R_3 are alkyl groups containing less than 7 carbon atoms. Preferably R_4 also contains less than 7 carbon atoms, with perhaps the best
15 compounds being those wherein R_4 is ethyl or methyl, and preferably ethyl.

Typical of the compounds of the present invention are the following:

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1. Bis ethyl mercury salt of ethylene diamine tetraacetic acid

2. Tetraethyl mercury salt of ethylene diamine tetraacetic acid

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3. Triethylmercury salt of ethylene diamine tetraacetic acid

4. Monoethyl mercury salt of ethylene diamine tetraacetic acid

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5. Bis ethyl mercury salt of hydroxyethyl ethylene diamine triacetic acid

6. Bis ethyl mercury salt of ethylene triamine pentaacetic acid

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7. Bis ethyl mercury salt of 1,2-diamino cyclohexane tetraacetic acid

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8. Bis ethyl mercury salt of triethylene tetramine hexaacetic acid

9. Bis ethyl mercury salt of dipropylene triamine pentaacetic acid

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10. Bis ethyl mercury salt of 1,12 dodecanediamine tetraacetic acid

11. Bis ethyl mercury salt of ditertiary butyl diamine tetraacetic acid

12. Bis ethyl mercury salt of 2,7-dimethyl-2,7-octanodiamine tetraacetic acid

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13. Bis ethyl mercury salt of 1,10-decanediamine tetraacetic acid

14. Bis ethyl mercury salt of 2,2-dimethyl-1,3-propanediamine tetraacetic acid

15. Bis methyl mercury salt of ethylene diamine tetraacetic acid

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16. Bis propyl mercury salt of ethylene diamine tetraacetic acid

17. Bis butyl mercury salt of ethylene diamine tetraacetic acid

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18. Bis hexyl mercury salt of ethylene diamine tetraacetic acid

19. Methyl mercury, butyl mercury salt of ethylene diamine tetraacetic acid

20 The fungicidally active compounds of the above-described type can be prepared by various means. For example, they can be prepared by reacting a polyamine polyacetic acid with an alkyl mercury salt or an alkyl

mercury hydroxide. They can also be prepared by reacting the polyamine polyacetic acids with mercuric oxide to form the corresponding mercuric salt and then reacting the mercuric salt with a dialkyl mercury to form the alkyl mercury salt. The polyamine polyacetic acid reactants used in these methods can be prepared by conventional means such as by reacting the polyamine with chloroacetic acid. The preparation of the polyamines themselves can be carried on by any conventional methods; many such polyamines are currently available on the market.

The above-described methods of preparing the compounds of the present invention frequently give mixtures of the mono-, di-, tri- and tetra-derivatives, with the relative proportions of these derivatives depending upon the reactants employed and the reaction conditions. These mixtures ordinarily are used as such in the fungicidal compositions and methods of the present invention, although they can be separated if desired.

In practicing the fungicidal methods of the present invention, one or more of the active ingredients is applied to the organic material to be treated for the control of fungi at a dosage sufficient to exert fungicidal action. Accordingly, the compositions and methods of the present invention are applicable for the protection of carbohydrates, proteins and fats. They are particularly suited for the treating of living plant matter such as vegetables, ornamental plants, fruit-bearing trees, turf and seeds. Some of these compositions are also effective when applied directly to the soil for controlling plant fungi. Also they can be used to treat organic fibers and fabrics and various cellulosic materials such as leather and wood. Likewise, they can be used to treat paints and lubricating oils.

In application to plants, fungicidal control is obtained in most instances by applying the active compound at a dosage or rate from about 0.01 to 5.0 lbs./acre, the optimum amount within this range being largely dependent upon the variables mentioned heretofore. In application directly to the soil for use as a fungicide, in most instances the dosage is from about .1 to 50 lbs./acre. In application to seeds as a seed disinfectant, the dosage ordinarily employed is from about .01 to .1 oz./bushel of seed. The optimum dosage can be determined in each instance by one of the means conventional in the art. It is, of course, determined by and dependent upon the particular fungicidal compound selected, the method of application, and, in the case of application to vegetation, the state and condition of growth of the vegetation to be treated and the climatic conditions.

As aforementioned, most of the compounds of the present invention are sufficiently water-soluble to apply from an aqueous medium. This is particularly true of the alkali metal, ammonium and substituted ammonium salts. However, in some instances it is desirable to apply these fungicides in the form of a fungicidal composition. These fungicidal compositions contain in sufficient amount to exert fungicidal action one or more of the above-described active compounds in admixture with a carrier material or conditioning agent of the kind used and commonly referred to in the art as a fungicide adjuvant or modifier. The conventional fungicide adjuvants are inert solids, organic liquid diluents and surface-active agents. They provide formulations adapted for ready and efficient application using conventional applicator equipment. Usually from about 1-95% by weight of the fungicidal composition is active ingredient.

Solid compositions are preferably in the form of powders. They are compounded to be homogeneous powders that can be either used as such, diluted with inert solids to form dusts, or suspended in a suitable liquid medium for spray application. The powders usually comprise active ingredient admixed with minor amounts of conditioning agent. Natural clays (either absorptive such as attapulgite or relatively non-absorptive such as

kaolin clays), diatomaceous earth, walnut shell flour, tobacco dust, redwood flour, synthetic fine silica, calcium silicate and other inert solid carriers of the kind conventionally employed in powder fungicidal compositions can be used. The active ingredient usually makes up from about 25-90% of these powder compositions. For conversion of the powders to dusts, talc, pyrophyllite, tobacco dust, volcanic ash and other dense, rapid-settling inert solids customarily are used.

Liquid compositions employing one or more of the fungicidally-active ingredients are prepared by admixing the active ingredient with a suitable liquid diluent medium. The active ingredient can be either in solution or in suspension in the liquid medium. Typical of the liquid media commonly employed as fungicide adjuvants are kerosene, Stoddard solvent, xylene, alcohols, alkylated naphthalene and glycols. The active ingredient usually makes up from about 0.5 to 50% of these liquid compositions. Some of these compositions are designed to be used as such, and others to be extended with large quantities of water.

Compositions in the form of wettable powders or liquids in many cases also include one or more surface-active agents such as wetting, dispersing or emulsifying agents. These materials cause the compositions to disperse or emulsify easily in water to give aqueous sprays.

The surface-active agents employed can be of the anionic, cationic or nonionic type. They include, for example, sodium oleate, sulfonated petroleum oils, alkyl aryl sulfonates, sodium lauryl sulfate, polyethylene oxides, lignin sulfonates, and other surface-active agents. A detailed list of such agents is set forth in an article by McCutcheon in "Soap and Chemical Specialties," volume 31 Nos. 7-10 (1955).

In some cases it may be desirable to employ the active compounds of the present invention in combination with other fungicides to give compositions that have broad spectrum fungicidal activity. In these mixtures, the fungicidally active materials can be present in any desired amount, ordinarily from about 0.1-20 parts by weight of a compound represented by Formula 1 per part by weight of the auxiliary fungicidally active material. In some instances it may even be desirable to employ two or more auxiliary fungicides.

Typical of the auxiliary fungicides that can be employed in combination with the compounds of the present invention are the following:

- N-trichloro-methylthio-4 - cyclohexene - 1,2-dicarboximide
- Tetramethylthiuram disulfide
- Manganese ethylene-bis-dithiocarbamate
- Ferric dimethyl dithiocarbamate
- Zinc ethylene-bis-dithiocarbamate
- Zinc dimethyl dithiocarbamate
- Tetra copper calcium oxysulfide
- Tetrachloro-p-benzoquinone
- 2,3-dichloro-1,4-naphthoquinone
- 2-dichloro-6-(o-chloroanilino)triazine
- Ethylene thiuram monosulfide
- 2-heptadecyl glyoxalidine acetate
- Ferric dimethyl dithiocarbamate plus 2-mercapto-benzothiazole
- Manganese dimethyl dithiocarbamate plus 2-mercapto-benzothiazole
- Copper dihydrazinium sulfate
- Copper-8-quinolinolate
- Cycloheximide
- Terramycin
- Sterptomycin

Also insecticides such as aldrin, dieldrin, endrin, heptachlor and chlordane can be included in these compositions.

In order that the invention may be better understood,

the following examples are given in addition to those already set forth above:

Example 1

Fifty grams of ethylene diamine tetraacetic acid are made into a paste with water and then 37.05 grams of mercuric oxide are added to the paste and mixed well. The mixture is warmed on a steam bath and stirred constantly for several hours during which time the yellow color of the mercuric oxide disappears and the composition turns entirely white. This monomercure derivative of ethylene diamine tetraacetic acid is made into a thin slurry with 300 ml. of methanol and then 44.2 grams of mercury diethyl is added slowly while stirring. During the addition of the mercury diethyl, the mixture thickens and more methanol is added to maintain a thin slurry. After all of the mercury diethyl has been added, the reaction mixture is warmed on a steam bath for several hours and is then allowed to evaporate to dryness. After drying to constant weight, the white crystals of bis ethyl mercury salt of ethylene diamine tetraacetic acid weigh 127 grams (100% yield equals 128.5 grams). The compound is slightly soluble in water, highly soluble in aqueous solutions of sodium hydroxide and ammonia, and after recrystallization from water gives a compound that softens at 141° C. and darkens on further heating.

Example 2

Fifteen grams of ethyl mercury acetate are dissolved in 200 ml. of water and then 7.6 grams of ethylene diamine tetraacetic acid are added in small portions at a time while warming the reaction mixture on a steam bath. At first the mixture forms a clear solution indicating some water solubility of the compound formed. When more of the ethylene diamine tetraacetic acid is added a crystalline product forms. After all of the ethylene diamine tetraacetic acid has been added the reaction mixture is warmed on the steam bath to complete the reaction. The aqueous portion is allowed to evaporate until about 100 ml. of water remains. The mixture is then cooled and the white crystals are filtered, washed with water and dried. 17.5 grams of white crystals are obtained. The compound obtained is bis ethyl mercury salt of ethylene diamine tetraacetic acid. These crystals are slightly soluble in water and highly soluble in aqueous solutions of NaOH and NH₃.

Example 3

The tetraethyl mercury salt of ethylene diamine tetraacetic acid is prepared by reacting the dimercure salt of ethylene diamine tetraacetic acid with mercury diethyl as follows:

Ten grams of ethylene diamine tetraacetic acid are mixed with 14.8 grams of mercuric oxide and then made into a paste by the addition of water. The mixture is warmed in a steam bath for several hours while being stirred. The yellow color of the mercuric oxide disappears and the reaction mixture becomes white. 17.7 grams of mercury diethyl are then added slowly to the water slurry of the dimercure derivative of ethylene diamine tetraacetic acid. A reaction takes place immediately as is evidenced by a rise in temperature. After all of the mercury diethyl has been added the mixture is held at about 60° C. for one hour and then finally heated to 80° C. until dry. 41 grams of a white crystalline compound are obtained. This compound is slightly soluble in water but very soluble in aqueous solutions of ammonia. Recrystallization from water gives a compound that softens at 129° C. but darkens on further heating.

Example 4

In accordance with the procedure of Example 2, the compounds given in the following table are made by

reacting one mole of the amino acetic acid with the indicated number of moles of the alkylmercury acetate:

Compound	Amino Acetic Acid	Alkyl Mercury Acetate
triethyl mercury salt of ethylene diamine tetraacetic acid.	ethylene diamine tetraacetic acid.	3 moles ethyl mercury acetate.
monoethyl mercury salt of ethylene diamine tetraacetic acid.	-----do-----	1 mole ethyl mercury acetate.
bis ethyl mercury salt of hydroxyethyl ethylene diamine triacetic acid.	hydroxy ethyl ethylene diamine triacetic acid.	2 moles ethyl mercury acetate.
Bis ethyl mercury salt of ethylene triamine pentaacetic acid.	ethylene triamine pentaacetic acid.	Do.
15 Bis ethyl mercury salt of 1, 2-diamino cyclohexane tetraacetic acid.	1, 2-diamino cyclohexane tetraacetic acid.	Do.
Bis ethyl mercury salt of triethylene tetramine hexaacetic acid.	triethylene tetramine hexaacetic acid.	Do.
20 Bis ethyl mercury salt of dipropylene triamine pentaacetic acid.	dipropylene triamine pentaacetic acid.	Do.
bis ethyl mercury salt of 1-12 dodecanediamine tetraacetic acid.	1-12 dodecanediamine tetraacetic acid.	Do.
bis ethyl mercury salt of ditertiary butyl diamine tetraacetic acid.	ditertiary butyldiamine tetraacetic acid.	Do.
25 bis ethyl mercury salt of 2, 7-dimethyl-2, 7-octane diamine tetraacetic acid.	2, 7-dimethyl-2, 7-octane diamine tetraacetic acid.	Do.
bis ethyl mercury salt of 1, 10-decanediamine tetraacetic salt.	1, 10-decanediamine tetraacetic acid.	Do.
bis ethyl mercury salt of 2, 2-dimethyl-1, 3-propanediamine tetraacetic acid.	2, 2-dimethyl-1, 3-propane diamine tetraacetic acid.	Do.
bis methyl mercury salt of ethylene diamine tetraacetic acid.	ethylene diamine tetraacetic acid.	2 moles methyl mercury acetate.
bis propyl mercury salt of ethylene diamine tetraacetic acid.	-----do-----	2 moles propyl mercury acetate.
35 bis butyl mercury salt of ethylene diamine tetraacetic acid.	-----do-----	2 moles butyl mercury acetate.
bis hexyl mercury salt of ethylene diamine tetraacetic acid.	-----do-----	2 moles hexyl mercury acetate.
40 methyl mercury, butyl mercury salt of ethylene diamine tetraacetic acid.	-----do-----	1 mole methyl mercury acetate and 1 mole butyl mercury acetate.

Example 5

The following aqueous formulations are prepared by stirring the listed ingredients together. These compositions are suitable for application using conventional seed treating apparatus.

A		G.
Bis ethyl mercury derivative of ethylene diamine tetraacetic acid.....		5.0
55 Sodium hydroxide.....		0.6
Water		47.2
Ethanol		47.2
B		
Bis ethyl mercury derivative of ethylene diamine tetraacetic acid.....		5.0
28% ammonia.....		1.0
Water		47.0
65 Ethanol		47.0
C		
Bis (ethylmercury) derivative of ethylene diamine tetraacetic acid.....		5.0
Sodium hydroxide.....		0.6
Water		47.2
Ethanol		10.0
Ethylene glycol.....		36.2
75 Rhodamine B dye.....		1.0

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These compositions, when applied to wheat, rye and oat seeds at the rate of ½ oz. of the active ingredients per bushel, give excellent protection to the seed against fungus attack.

Example 6

The following dust formulations are prepared by blending the listed ingredients and grinding them to a particle size substantially less than 20 microns.

A		G.
Bis ethyl mercury derivative of ethylene diamine tetraacetic acid.....	5.0	
Dusting talc.....	95.0	
B		
Bis ethyl mercury salt of ethylene diamine tetraacetic acid.....	25.0	
Attapulgit clay	75.0	
C		
Tetraethyl mercury derivative of ethylene diamine tetraacetic acid.....	10.0	
Dusting talc.....	45.0	
Diatomaceous earth.....	45.0	

D

Bis ethyl mercury salt of hydroxyethyl ethylene diamine triacetic acid.....	5.0
Dusting talc.....	47.5
China clay.....	47.5

E

Bis ethyl mercury salt of diethylene triamine pentaacetic acid.....	5.0
Dusting talc.....	95.0

F

Monoethyl mercury salt of ethylene diamine tetraacetic acid.....	10.0
Pyrophyllite	90.0

These compositions, when applied to wheat seed, give excellent disinfectant action. The formulations containing 5% active are applied at the rate of ½ oz./bu.; the 10% formulations at ¼ oz./bu.; and the 25% formulation at .1 oz/bu.

Example 7

The following dispersible powder formulations are prepared by blending together the listed ingredients and grinding to a particle size substantially less than 10 microns.

A		G.
Tetraethyl mercury derivative of ethylene diamine tetraacetic acid.....	4.1	
Sodium lignin sulfonate.....	2.0	
Alkyl aryl sodium sulfonate.....	1.0	
China clay.....	92.9	
B		
Bis ethyl mercury salt of ethylene diamine tetraacetic acid.....	10.0	
Sodium lignin sulfonate.....	3.0	
Sodium lauryl sulfate.....	0.5	
Attapulgit clay.....	86.5	
C		
Bis ethyl mercury salt of hydroxy ethyl ethylene diamine triacetic acid.....	40.0	
Sodium naphthalene sulfonate-formaldehyde condensation product.....	1.0	
Alkyl aryl polyether alcohol.....	1.0	
Diatomaceous earth.....	58.0	

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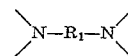
D

Mono ethyl mercury salt of ethylene diamine tetraacetic acid.....	25.0
Methyl cellulose.....	1.0
Alkyl aryl sodium sulfonate.....	1.0
Diatomaceous earth.....	25.0
China clay.....	48.0

These compositions when applied as a spray to apple foliage 48 hours after infection by apple scab (*Venturia inaequalis*) will effect a cure of infection. The 10% active formulation is used at a rate of ⅓ to ¼ pound per 100 gallons and the other formulations are used at equivalent rates of active ingredient. For example, only ¼ as much of the 40% formulation would be required to give the same amount of active ingredient as the 10% formulation.

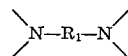
What is claimed is:

1. The method for the control of fungi on plants, seeds, leather, wood, organic fabrics and fibers, and in soil, paints, and lubricating oils, comprising applying to a said material to be protected an alkyl mercury salt of polyamine acetic acid wherein the polyamine group is represented by the structure



in which R₁ is selected from the group consisting of divalent saturated hydrocarbon groups of from 2 through 12 carbon atoms and divalent saturated aliphatic chains consisting of from 4 through 12 carbon atoms and from one through 5 nitrogen atoms with each nitrogen atom dividing the chain into alkylene groups of not less than 2 carbon atoms each; from 1 through 4 valences of the polyamine nitrogens being satisfied by an alkylmercury acetate group of the type —CR₂R₃COOHgR₄ in which R₂ and R₃ are selected from the group consisting of hydrogen and alkyl groups of less than 7 carbon atoms, and R₄ is an alkyl group; and the remainder of the valences of the polyamine nitrogens being satisfied by radicals selected from the group consisting of hydrogen, alkyl groups of less than 7 carbon atoms, hydroxyalkyl groups of less than 7 carbon atoms and —CR₂R₃COOY in which R₂ and R₃ have the significance set forth above and Y is selected from the group consisting of hydrogen, alkali metal cations, ammonium or substituted amine.

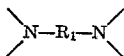
2. A fungicidal composition comprising a fungicidal adjuvant, and an alkyl mercury salt of polyamine acetic acid wherein the polyamine group is represented by the structure



in which R₁ is selected from the group consisting of divalent saturated hydrocarbon groups of from 2 through 12 carbon atoms and divalent saturated aliphatic chains consisting of from 4 through 12 carbon atoms and from one through 5 nitrogen atoms with each nitrogen atom dividing the chain into alkylene groups of not less than 2 carbon atoms each; from 1 through 4 valences of the polyamine nitrogens being satisfied by an alkyl mercury acetate group of the type —CR₂R₃COOHgR₄ in which R₂ and R₃ are selected from the group consisting of hydrogen and alkyl groups of less than 7 carbon atoms, and R₄ is an alkyl group of less than 7 carbon atoms; and the remainder of the valences of the polyamine nitrogens being satisfied by radicals selected from the group consisting of hydrogen, alkyl groups of less than 7 carbon atoms, hydroxyalkyl groups of less than 7 carbon atoms and —CR₂R₃COOY in which R₂ and R₃ have the significance set forth above and Y is selected from the group consisting of hydrogen, alkali metal cations, ammonium or substituted amine.

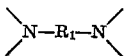
3. A fungicidal composition comprising a water-glycol alcohol solution of an alkyl mercury salt of polyamine

acetic acid wherein the polyamine group is represented by the structure.



in which R_1 is selected from the group consisting of divalent saturated hydrocarbon groups of from 2 through 12 carbon atoms and divalent saturated aliphatic chains consisting of from 4 through 12 carbon atoms and from one through 5 nitrogen atoms with each nitrogen atom dividing the chain into alkylene groups of not less than 2 carbon atoms each; from 1 through 4 valences of the polyamine nitrogens being satisfied by an alkyl mercury acetate group of the type $-\text{CH}_2\text{R}_3\text{COOHgR}_4$ in which R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups of less than 7 carbon atoms, and R_4 is an alkyl group of less than 7 carbon atoms; and the remainder of the valences of the polyamine nitrogens being satisfied by radicals selected from the group consisting of hydrogen, alkyl groups of less than 7 carbon atoms, hydroxyalkyl groups of less than 7 carbon atoms and $-\text{CR}_2\text{R}_3\text{COOY}$ in which R_2 and R_3 have the significance set forth above and Y is selected from the group consisting of hydrogen, alkali metal cations, ammonium or substituted amine.

4. A fungicidally active compound represented by the formula



in which R_1 is selected from the group consisting of divalent saturated hydrocarbon groups of from 2 through 12 carbon atoms and divalent saturated aliphatic chains consisting of from 4 through 12 carbon atoms and from one through 5 nitrogen atoms with each nitrogen atom dividing the chain into alkylene groups of not less than 2 carbon atoms each; from 1 through 4 valences of the polyamine nitrogens being satisfied by an alkyl mercury acetate group of the type $-\text{CH}_2\text{R}_3\text{COOHgR}_4$ in which R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups of less than 7 carbon atoms, and R_4 is an alkyl group of less than 7 carbon atoms; and the remainder of the valences of the polyamine nitrogens being satisfied by radicals selected from the group consisting of hydrogen, alkyl groups of less than 7 carbon atoms, hydroxyalkyl groups of less than 7 carbon atoms and $-\text{CR}_2\text{R}_3\text{COOY}$ in which R_2 and R_3 have the significance set forth above and Y is selected from the group consisting of hydrogen, alkali metal cations, ammonium or substituted amine.

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Hopf: Chem. Abstr. 48: 542 7f.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,898,262

August 4, 1959

Harry F. Dietz, deceased, by Dorothy H. Dietz, executrix

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 39, after "group" insert -- of less than 7 carbon atoms --; column 10, line 9, for " $-\text{CH}_2\text{R}_3\text{COOHgR}_4$ " read -- $-\text{CR}_2\text{R}_3\text{COOHgR}_4$ --.

Signed and sealed this 9th day of February 1960.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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